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Modification of Flexible Part in Cu^{2+} Interdigitated Framework for CH_4/CO_2 Separation

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The structural flexibility of Cu^{2+} interdigitated layer type framework was controlled and the compound represented clear separation property of CO_2/CH_4 at range of 0 ~ 1.0 MPa and recovery of adsorbed CO_2 above 0.1 MPa.

Development of materials and technology for selective adsorption of CO_2 gas from CO_2/CH_4 mixture has been a significant challenge in the area of natural-gas processing. Regarding to the porous materials for selective CO_2 capture from CO_2/CH_4 mixture, we could employ either kinetic and equilibrium based separation.[1] Activated carbon or zeolites have been mainly studied as equilibrium-based adsorbents and the main drawbacks are either low selectivity or regenerability. For a porous material design, we have to control gas sorption isotherms and some points are required. First, desorption pressure of CO_2 is related to the energy of CO_2 recovery and it should not be lower than 0.1 MPa otherwise we need to vacuum to regenerate the CO_2. Second, the separation ability should be observed in wide range of pressure (~1.0 MPa) for various types of pressure-swing processes. Especially the materials are required not to adsorb CH_4 at all in the pressure range mentioned above.

Porous coordination polymers (PCPs) or metal-organic framework (MOFs) constructed from metal cations and organic linkers are a new class of microporous materials that show promise for gas separation applications because of their structural versatility.[2-7] Especially the PCPs whose structures have flexible nature are attracting due to their potential applications in gas separation with unique mechanisms.[8, 9] They represent a reversible transformation of open/close frameworks accompanied by guest sorption processes and it is often sensitive to the specific guest molecule.[8, 10-12]

Extended frameworks constructed from two-dimensional (2D) layers have been widely studied because they can accommodate various guest molecules in the interlayer spaces.[13, 14] Likewise, 2D PCPs are significant motif for selective gas adsorption because we could tune the flexibility of layer-layer interaction and intrinsic flexibility of coordination bond.[15, 16] Rational design of PCP framework has encouraged us for an optimization of gas separation performance especially the capture of CO_2 gas from CO_2/CH_4 mixture at ambient condition. Herein we demonstrate a modification of flexibility in 2D PCP framework by ligand design and control the adsorption isotherms of CO_2 and CH_4 to give idea for optimization of gas separation property.

Previously we reported a flexible 2D PCP; $[Cu(dhbc)_2(4,4'\text{-bpy})]\cdot H_2O$ (**1⊃H_2O**) where Hdhbc = 2,5-dihydroxybenzoic acid and bpy = 4,4'-bipyridyl of which represents various "gate-opening" type gas adsorption profiles.[17, 18] Several gas adsorption at 298 K were reported and to carefully investigate the adsorption behavior at below 1 MPa, the CO_2 and CH_4 adsorption isotherms of **1** at 273 K were measured as shown in Figure 1c. It starts to adsorb CO_2 at P = 0.04 MPa and CH_4 at 0.65 MPa. Many flexible PCPs including **1** adsorb CO_2 below 0.1 MPa and CH_4 below 1.0 MPa and the compounds are not satisfactory for CO_2/CH_4 separation with low energetic cycle. To elucidate the structural contribution for the gas adsorption profiles, we characterized the crystal structure of guest-free **1**. Careful degas treatment of single crystal of **1⊃H_2O** gave the closed structure of **1** (Figure 1a and b).

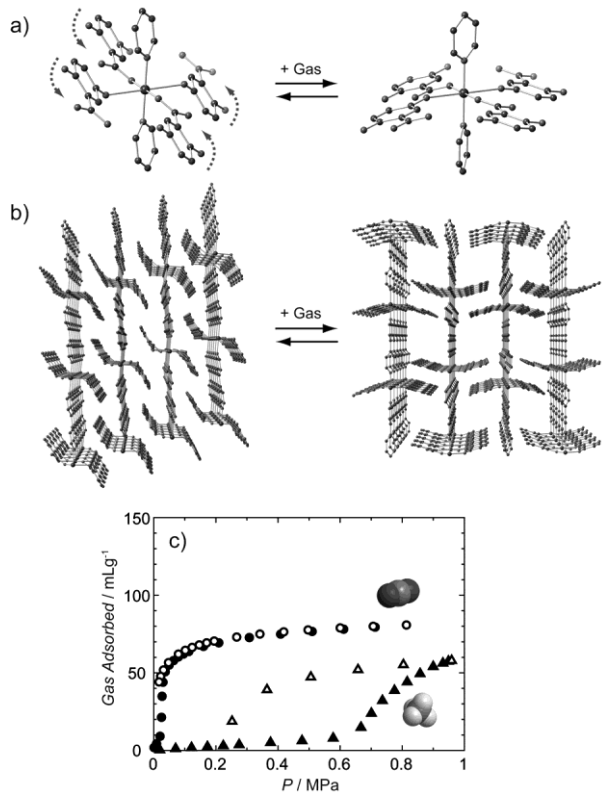

Figure 1. Representations of crystal structure transformation of **1** and **1⊃H_2O** (a) environment around the Cu^{2+} ions and (b) 2D layer stacking motif with/without guest molecules. Guests are omitted. (c) Adsorption and desorption isotherms of CO_2 (open and closed circles) and CH_4 (open and closed triangles) for **1** at 273 K.

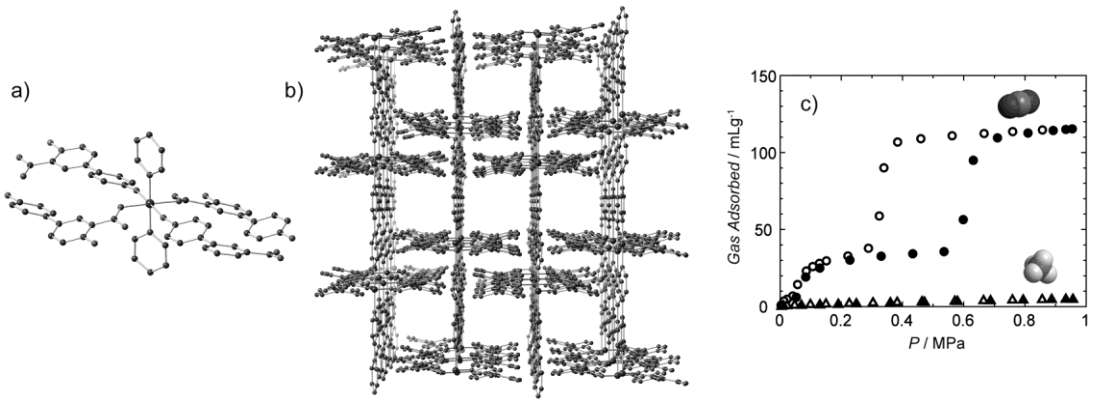

Figure 2. Representation of crystal structures of **2** (a) around the Cu^{2+} ion and (b) 2D layer stacking. Guests are omitted. (c) Adsorption and desorption isotherms of CO_2 (open and closed circles) and CH_4 (open and closed triangles) for **2** at 273 K.

Although the coordination environment around the Cu^{2+} ion is not different compared with **1⊃H$_2$O**, the benzene rings of dhbc ligand largely tilt because of the bending of coordination bonds (Cu-O) in carboxylate and hydroxy groups. Two dhbc ligands have *trans*-type fashion around the Cu^{2+} ion, whereas they have *cis*-type fashion in original phase (**1⊃H$_2$O**). The local reorientation affects the stacking of 2D layers and the networks are densely packed resulting the guest accessible void volume of 2.1%.[19] This means the structural transformation is "porous" (**1⊃H$_2$O**) to "nonporous" (**1**) and it causes the gate-opening type adsorption behavior for various gasses.[12, 20]

The **1** has high flexibility in the part of dhbc because of the coordination bond with hydroxy group and the size of ligand and it promotes the overall transformation. The structural transformation had low activation energy and afforded the favorable adsorptions of CO_2 and CH_4 at low pressure at 273 K. To shift the gate-opening pressure of CO_2 above 0.1 MPa and avoid CH_4 adsorption in the pressure range of zero to 1 MPa, we prepared an interdigitated framework by employing the 4,4'-dihydroxybiphenyl-3-carboxylic acid (H_3dhbpc) as a ligand.[21] The H_3dhbpc can be regarded as an elongated version of dhbc ligand in **1** and the enlargement of the ligand could promote a lower flexibility in the 2D layers because of an increase of activation energy for structural transformation. The H_3dhbpc was synthesized according to the literature method.[21] Slow diffusion of $Cu(NO_3)_2{\cdot}3H_2O$ and H_3dhbpc with bpy in acetone and water solution formed green single crystal $[Cu(dhbpc)_2(4,4'\text{-bpy})]{\cdot}2$Acetone (**2⊃Acetone**) and the crystal structure is shown in Figure 2a and 2b. The framework has similar motif with **1⊃H$_2$O** and the dhbpc replace the positions of dhbc to form an interdigitated framework. The coordination environment around the Cu^{2+} center is octahedral coordinated to dhbpc and bpy and the dihedral angle of benzene rings in dhbpc is 34.0°. The Cu^{2+} and dhbpc and bpy form 2D layers and each layers is stacked with interdigitated fashion containing two acetone molecules as guests. The void volume of the framework of **2⊃Acetone** is 20% and it is comparable to the **1⊃H$_2$O**. We have not determined the crystal structure of degassed **2** because of large transformation confirmed by powder X-ray measurement but clearly it showed reversible transformation via guest accommodation and release. We refined the cell parameters of guest-free **2** from XRD pattern by LeBail fitting and the refined values are different from that of **2⊃Acetone** which indicates the large structural transformation. We could expect higher activation energy from close to open phase than **1** if the **2** has similar reorientation around the Cu^{2+} atoms with **1** because of the size of dhbpc ligand. Thermogravimetric analysis of guest-free **2** supported a thermal stability of the framework until 500 K.

The **2** represented different type of gas adsorption profiles from **1**. For CO_2 adsorption at 273 K, the **2** represented double stepwise adsorption (Figure 2c). Initial gas uptake was at 0.04 MPa and first uptake occurred to reach saturation (34 mLg^{-1}). The plateau appears in the range of 0.20~0.55 MPa and moved to next uptake to the second saturation point (115 mLg^{-1}). To obtain structural information, we studied simultaneous measurement of CO_2 adsorption and powder X-ray diffraction at 195 K to investigate the structural information via adsorption at each plateau. The XRD pattern at P = 3.9 kPa is slighly different from degassed **2** indicating the presence of metastable phase of structure. As the pressure increases, the second step occurs and is attributed by the transformation to reach the stable structure which is similar with **2⊃Acetone**.[15] From the measurement, we could pursue the stepwise transformations of structure of **2**. The bulkiness of dhbpc ligand would not permit to give perfect nonporous stacking of layer structure like **1** and it results the initial microporosity. In desorption process, the adsorbed CO_2 at second step (total 81 mLg^{-1}) was released at P = 0.4 MPa which was higher than 0.1 MPa and that of **1**. It is desirable for the regeneration of CO_2 from adsorbed phase.

The stepwise adsorption behavior was also observed in H_2O adsorption at 298 K. Although **1** represented single gate-opening type adsorption at 2.2 kPa, **2** gave gradual uptake until P = 2.2 kPa and second jump was observed. Both compounds had large hysteresis in desorption curves which was indicative of stabilization of water molecule in the pores. The final adsorption amount of CO_2 for **2** is 1.5 times larger than that of **1** and comparable to the other adsorbents.[22-24] The low flexibility in **2** also affected an isotherm of CH_4. The **2** provided negligible amount of uptake for CH_4 even at

pressure of 1.0 MPa at 273 K. Although the **1** gradually adsorbs CH_4 until P = 0.65 MPa (10 mLg^{-1}, Figure 1c) and shows abrupt uptake to reach 58 mLg^{-1} at 0.95 MPa, the **2** adsorbs only 4 mLg^{-1} at 1.0 MPa resulting the better selectivity on CH_4/CO_2. The low flexiblity of **2** for CH_4 is unique for creation of repulsive property against the CH_4 molecule at wide pressure range. It provides another idea of PCPs/MOFs for CH_4/CO_2 separation with other metal-organic frameworks having rigid porous scaffold and preferable binding character for CO_2 gas.[25-27]

We checked the separation ability of CO_2 over CH_4 from CH_4/CO_2 mixture gas and executed the co-adsorption measurement by use of our hand-made instrument. We dosed mixture gas (CH_4:CO_2 = 1:1(vol)) for **2** under the condition of total pressure 0.1 MPa and 273 K then hold three hours to wait the equilibrium co-adsorption process and detected the adsorbed gas species by gas chromatography. Although the total adsorbed amount of gas was low (17 mLg^{-1}) because of the low total pressure in this measurement, we hardly observed the trace of CH_4 which indicated the all the adsorbed gas was CO_2 and we observed clear separation property for CO_2 from mixture gas. The adsorption is corresponding to the first uptake of CO_2 for **2** in Figure 2c. Take the single adsorption isotherms of CO_2 and CH_4 into consideration, the compound **2** is expected to show high separation ability in wide range of pressure, especially above 0.1 MPa. Evaluation of separation performance from mixture gas at higher pressure and temperature is under investigation.

Based on the crystallographic information of **1**, we enlarged the size of flexible ligand for tuning of activation energy of structural transformation and gave suitable flexibility for CH_4/CO_2 separation at the total pressure of zero to 1.0 MPa. The **2** releases adsorbed CO_2 above 0.1 MPa and it allows gas recovery without vacuum. The flexibility herein is the combination of layer-layer interaction and local flexibility of coordination bonds in the layer and the approach is feasible only if we employ the 2D porous coordination layer.

In conclusion, we demonstrated that the minor modification of the ligand moiety in the layer framework causes a remarkable change in the gas adsorption properties, which is relevant for appropriate gas separation condition with low energy consumption process.

Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis, elemental analysis, TGA curve, XRPD patterns with LeBail fitting, H_2O adsorption/desorption isotherms, simultaneous measurements of CO_2 adsorption and XRPD measurement. CCDC reference numbers 776333 (**1**) and 776334 (**2⊃Acetone**).See DOI: 10.1039/b000000x/

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